[Contribution from the Department of Chemistry and Chemical Engineering, Stanford University]

Peroxides. VIII. The Mechanism for the Thermal Decomposition of *n*-Butyl Hydroperoxide and *n*-Butyl 1-Hydroxybutyl Peroxide[1]

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A study of the liquid phase, thermal decomposition of primary hydroperoxides to give hydrogen and the corresponding acid, $RCH_2OOH \rightarrow RCOOH + H_2$, indicates that an alkyl 1-hydroxyalkyl peroxide serves as an intermediate. This intermediate is formed from the hydroperoxide and the aldehyde *in situ*, $R\text{-}CH_2OOH + RCHO \rightarrow R\text{-}CH_2OOCHOHR$. The evidence implicating this intermediate is reviewed and the mechanism whereby it decomposes has been postulated. The products of the reaction, deuterium exchange experiments, and effects of acid, base and ultraviolet light are interpreted in terms of a unimolecular decomposition *via* a cyclic transition state in a concerted manner which produces molecular and not atomic hydrogen.

In the preceding paper in this series[3] it was observed that the decomposition of *n*-butyl hydroperoxide, to give butyric acid and hydrogen, was accompanied by an induction period which was

$$R\text{-}CH_2OOH \longrightarrow RCOOH + H_2 \qquad (1)$$

eliminated by the addition of aldehydes. This suggested the possibility that the reaction product between an aldehyde and the hydroperoxide was an intermediate. We therefore undertook a study of the reaction of primary hydroperoxides and aldehydes and of the decomposition of the reaction products.

It is desirable to review what has been reported concerning this type of intermediate and in general concerning any peroxide decompositions which are known to give substantial amounts of hydrogen on thermal, liquid phase decomposition. The first report of hydrogen evolution from a peroxide was by Blank and Finkenbeiner[4] for the reaction of formaldehyde, hydrogen peroxide and sodium hydroxide to give hydrogen and sodium formate. This was developed into a quantitative method for the determination of formaldehyde. This reaction

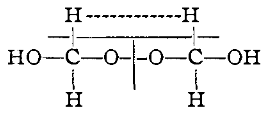
$$2CH_2O + H_2O_2 + 2NaOH \longrightarrow H_2 + 2HCOONa + 2H_2O \qquad (2)$$

was investigated further by Wieland and Wingler[5] who postulated that bis-(hydroxymethyl) peroxide, a crystalline compound synthesized earlier by Fenton[6] from hydrogen peroxide and formaldehyde according to eq. 3, was in fact an intermediate in the Blank–Finkenbeiner reaction and decomposes according to eq. 4.

$$H_2O_2 + 2CH_2O \longrightarrow HOCH_2OOCH_2OH \qquad (3)$$

$$2NaOH + HOCH_2OOCH_2OH \longrightarrow 2HCOONa + H_2 + 2H_2O \qquad (4)$$

Wieland and Wingler[5] represented this decomposition as follows in which it was considered that the hydrogen was evolved as molecular hydrogen.[7]



$$\begin{array}{c}\mathrm{H}\text{-}\text{-}\text{-}\text{-}\text{-}\text{-}\text{-}\text{-}\text{-}\text{-}\text{-}\text{-}\mathrm{H}\\ \mathrm{HO{-}\underset{\displaystyle H}{C}{-}O{-}O{-}\underset{\displaystyle H}{C}{-}OH}\end{array}$$

This was based in part on their observation that the decomposition mixture did not decolorize a solution of methylene blue. They showed that the reaction was base-catalyzed but that in the absence of base the pure bis-(hydroxymethyl) peroxide evolved 66–85% of the theoretical amount of hydrogen (as compared to the theoretical amount in the presence of base). In the absence of base they found evidence for the competing reaction

$$HOCH_2OOCH_2OH \longrightarrow HCOOH + HCHO + H_2O \qquad (5)$$

Many higher bis-(1-hydroxyalkyl) peroxides have been made,[5,8a] but there seems to be no report of their undergoing either thermal or base-catalyzed decomposition to give hydrogen in appreciable amounts.[9] There have been several subsequent studies on the mechanism of the Blank–Finkenbeiner reaction.[10] There seems to be no serious question concerning the intermediacy of the bis-(hydroxymethyl) peroxide, but the mechanistic details for its decomposition are still unsettled.

Rieche and Hitz[11] have reported that methyl hydroperoxide decomposed explosively upon heating and that alkaline solutions started to decompose suddenly at about 70° with the evolution of almost pure hydrogen; formate ion and methanol were the main products in the residual liquid. They noted that this reaction was accelerated by the addition of formaldehyde. Rieche[8b] pointed out the similarity to the Blank–Finkenbeiner reaction and postulated that the base-catalyzed decomposition of methyl hydroperoxide proceeded *via* methyl hydroxymethyl peroxide formed by the addition of methyl hydroperoxide to formaldehyde in accordance with eq. 7. Although the type decomposition proposed by Wieland and Wingler for

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[1] Presented at the Gordon Research Conferences, Petroleum Section, June, 1956.

[2] Taken in part from the Ph.D. Thesis of C. F. W., Stanford University, 1957.

[3] C. F. Wurster, L. J. Durham and H. S. Mosher, This Journal, **80**, 327 (1958).

[4] O. Blank and H. Finkenbeiner, *Ber.*, **31**, 2979 (1898).

[5] H. Wieland and A. Wingler, *Ann.*, **431**, 301 (1923).

[6] H. J. J. Fenton, *Proc. Roy. Soc.* (*London*), **A90**, 492 (1914).

[7] From their discussion it is quite clear that they considered that the hydrogen–hydrogen bond was formed simultaneously with the breaking of the carbon–hydrogen bonds. [". . . . ehe das molekular Kraftfeld überschitten ist."] Nothing is mentioned, however, concerning the role of base in this decomposition.

[8] A. Rieche, "Alkylperoxyde und Ozonide," Theodor Steinkopff, Dresden und Leipzig, 1931; (a) pp. 48–60; (b) pp. 16–21; (c) pp. 23–26.

[9] In spite of the report by Wieland and Wingler that not a trace of hydrogen was evolved from bis-(1-hydroxyethyl) peroxide in the presence or absence of base, we have found that this compound gave approximately a 5% yield of hydrogen on thermal decomposition at 100°. In addition bis-(1-hydroxybutyl) peroxide gave a 29% yield of hydrogen under these conditions.

[10] (a) J. B. Jaillet and C. Quellet, *Can. Chem. J.*, **29**, 1046 (1951); (b) K. Wirtz and K. F. Bonhoeffer, *Z. physik Chem.*, **B32**, 108 (1936); (c) S. Lenher, This Journal, **53**, 3737 (1931).

[11] A. Rieche and F. Hitz, *Ber.*, **62**, 2458 (1929).

bis-(hydroxymethyl) peroxide (in which the evolution of molecular hydrogen was postulated) was considered by Rieche, he rejected this in favor of the following radical mechanism primarily because the decomposition mixture was observed to decolorize methylene blue indicating the formation of active or atomic hydrogen.

$$2CH_3OOH \longrightarrow 2CH_2O + 2H_2O \quad (6)$$

$$2CH_3OOH + 2H_2CO \longrightarrow 2CH_3OOCH_2OH \quad (7)$$

$$2CH_3OOCH_2OH \longrightarrow 2CH_3O + 2HCOOH + 2H \quad (8)$$

$$2CH_3O \longrightarrow CH_3OH + HCHO \quad (9)$$

Since the formaldehyde is consumed in reaction with more hydroperoxide according to eq. 7, this series of reactions satisfactorily explains the products and their approximate relative proportions. The role of base in this sequence of reactions was not considered.

Ethyl hydroperoxide was reported by Rieche[8c] to decompose on heating with alkali, but in contrast to methyl hydroperoxide very little gas was evolved unless formaldehyde was added, in which case hydrogen was formed. Rieche postulated that ethyl hydroxymethyl peroxide was the intermediate and that the decomposition proceeded by the same sequence as eq. 7, 8 and 9 except the ethyl group replaced the methyl group. Methyl hydroxymethyl peroxide and ethyl hydroxymethyl peroxide were prepared[12] and reported to decompose on heating with alkali as predicted to give in the first case, hydrogen, formic acid and methanol, and in the second case, hydrogen, formic acid, ethanol and acetaldehyde. In contrast to this Rieche[12] reported that methyl 1-hydroxyethyl peroxide and ethyl 1-hydroxyethyl peroxide were decomposed by base but very little gas was evolved. No mention was made of simple thermal decomposition.

A subsequent report[13] has shown that hydrogen is formed when the R group in formula II is the secondary 1-tetrahydronaphthyl group. In addition, the compound where R is *t*-butyl in formula II has been prepared[14] and it is reported in the patent without further details that on heating with bases a gas is evolved which contains hydrogen and methane. It is apparent that there is considerable evidence concerning the liquid phase base-catalyzed decomposition of primary alkyl hydroperoxides and 1-hydroxyalkyl peroxides but very little concerning the simple thermal liquid phase decompositions which give hydrogen in substantial amounts. We therefore undertook a more detailed investigation into the mechanism of decomposition of *n*-butyl 1-hydroxybutyl peroxide and related substances and the relationship of this compound to the decomposition of *n*-butyl hydroperoxide.

$$R{\cdot}OOCH_2OH$$

II, $R = CH_3$, $-C_2H_5$, $-CH_2OH$, $-C(CH_3)_3$, 1-tetrahydronaphthyl

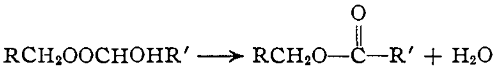
It has been found that *n*-butyl hydroperoxide reacts rapidly with butyraldehyde at room temperature and below to give *n*-butyl 1-hydroxybutyl peroxide, a peroxyhemiacetal (equation 10, R = n-C_3H_7), as expected from the work of Rieche[12] and Dickey.[14]

$$n\text{-}C_3H_7CH_2OOH + RCHO \longrightarrow n\text{-}C_3H_7CH_2OOCHOHR \quad (10)$$

The results of the decomposition of *n*-butyl 1-hydroxybutyl peroxide at 86° as the neat liquid are reported in Table I. The major products are hydrogen, butyric acid, butyraldehyde, butyl alcohol and butyl butyrate. The remainder of the products, such as propane, carbon monoxide, butyl formate, butyl propionate and propyl butyrate represent fragmentation and are produced in relatively small amounts. They presumably result from radical decompositions and because of their minor nature will not be considered further. With such a mixture of products this hardly can be classed as a simple reaction.

The compounds obtained in this decomposition and in that of *n*-butyl hydroperoxide were identical. With the exception of the yield of water, which apparently was much lower, and the yield of butyraldehyde, which was much higher, the quantitative amounts of these products were very similar. As a working hypothesis it was assumed that these major products arose primarily from the following two competing reactions in which the hydrogen,

$$R{-}CH_2OOCHOHR' \longrightarrow RCHO + R'COOH + H_2 \quad (11)$$



$$RCH_2OOCHOHR' \longrightarrow RCH_2O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + H_2O \quad (12)$$

butyric acid and butyraldehyde resulted from one mode of decomposition (represented by eq. 11) and the butyl butyrate arose from a second mode of decomposition (represented by eq. 12). The first of these reactions requires the production of equal molar amounts of the three products. As seen from the first column of Table I, the ratio observed for hydrogen, butyric acid and butyraldehyde was 52:76:27. It is possible to rationalize these results with equation 11 in several ways. If butyraldehyde underwent a disproportionation reaction to butyric acid and butyl alcohol, the butyraldehyde would be reduced by an amount equal to the butyl alcohol produced. Assuming that all of the butyl alcohol arose from such a reaction, the corrected ratio would be 52:53:50. Alternatively, the butyraldehyde could be converted to butyric acid by a radical reaction involving the hydroperoxide.[15]

It is proposed that *n*-butyl hydroperoxide, when heated as the neat liquid, decomposes to give hydrogen by the following route: Initially some *n*-butyl hydroperoxide decomposes relatively slowly to give *n*-butyraldehyde, presumably according to eq. 13.

$$RCH_2OOH \longrightarrow RCHO + H_2O \quad (13)$$

This is a reaction which has been postulated pre-

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[12] A. Rieche, *Ber.*, **63**, 2642 (1930).

[13] K. I. Ivanov, V. K. Savinova and E. G. Mikhailova, *J. Gen. Chem.* (*USSR*), **8**, 51 (1938); *C. A.*, **32**, 5393 (1938).

[14] F. H. Dickey, U. S. Patent 2,400,041, May 7, 1946.

(15) This discrepancy is being investigated further. Preliminary experiments show that addition of radical inhibitors such as hydroquinone do not affect appreciably the volume of hydrogen evolved but do change the ratio of butyric acid, butyraldehyde and butanol considerably. Since oxygen is not formed, the butyraldehyde cannot be directly oxidized to butyric acid during the reaction, but it is possible that the composition of the liquid products changes appreciably on standing after the decomposition and prior to analysis. These findings will be reported in a subsequent paper dealing with the kinetics of this decomposition.

TABLE I

PRODUCTS FROM THE DECOMPOSITION OF ALKYL 1-HYDROXYALKYL PEROXIDES[a]

Component	BuOOCHOHPr[b] 86°, Pyrex	BuOOCHOHPr[b] 86° quartz[c]	BuOOCHOHPr[b] 10%, TSA[e] 86°, Pyrex	BuOOCHOHPr[b] u.v. light[f] 35° quartz	BuOOCH_2OH[g] 86°, Pyrex	BuOOCHOHMe[d] 86°, Pyrex
Gas analyses						
Hydrogen	0.52	0.54	0.11	0.02	0.77	0.42
Propane and methane	.13	.13	.10	.29	.016	.10
Carbon monoxide	.12	.11	.02	.049	.055	.051
Carbon dioxide	.020	.015	.02	.085	.010	.066[d]
Oxygen	..	.002	.00	.004	..	.001
Liquid analyses						
n-Butyric acid	0.76	[c]	0.02	0.26	0.15	0.30
Water	.06		.68	..	.17	..
n-Butyl *n*-butyrate	.24		.42	0.12	.05	0.15
n-Butyraldehyde	.27		.12	.12	.34	.13
n-Butyl alcohol	.23		.23	.43	.06	.12
n-Butyl formate	.05		.23	.45	.22	.03
n-Butyl propionate and *n*-propyl butyrate	.02			.02	..	..

[a] Product analyses are given in mole per mole of hydroperoxide decomposed. Unless otherwise stated, decompositions were conducted in Pyrex bulbs. No induction period in the rate of gas evolution was observed in any of these examples. [b] BuOOCHOHPr represents *n*-butyl 1-hydroxybutyl peroxide. [c] Decomposed as the neat liquid in a fused silica bulb at 86°. Gas partition chromatography showed the liquid from this decomposition to have substantially the same composition as that resulting from the decomposition in a Pyrex bulb. [d] BuOOCHOHMe represents *n*-butyl 1-hydroxyethyl peroxide. In addition to the liquid products listed, 0.22 mole/mole of *n*-butyl acetate, 0.19 mole/mole of acetic acid, were isolated; approximately 25% of the liquid fraction was not positively identified. In the gas analysis, the acetaldehyde present was polymerized by the potassium hydroxide scrubber and the 0.066 value for CO_2 includes both CO_2 and acetaldehyde. [e] This decomposition was conducted in the presence of 10 weight per cent. of toluenesulfonic acid. [f] Decomposed as the neat liquid at 25–35° in a fused silica bulb by the radiation from a 2536 Å. light source. [g] BuOOCH_2OH represents *n*-butyl hydroxymethyl peroxide. In addition to the liquid products listed, 0.41 mole/mole of formic acid was present. About 15% of the liquid products was not identified. Since water and formic acid were not separated completely by the gas partition column used, these analytical figures are subject to greater error than for the other liquid components.

viously for the decomposition of primary and secondary hydroperoxides[10,16,17] and is one of the "expected" modes of decomposition for primary hydroperoxides. It is then postulated that as soon as it is formed, the *n*-butyraldehyde reacts by addition with the *n*-butyl hydroperoxide to give butyl 1-hydroxybutyl peroxide according to eq. 10, giving the analogous intermediate to that postulated by Rieche[8b] in the base-catalyzed decomposition of methyl and ethyl hydroperoxides. This peroxyhemiacetal then decomposes according to eq. 11, at a substantially faster rate than the initiation step (eq. 10), to give hydrogen, butyric acid and butyraldehyde. This differs from the sequence proposed by Rieche[8b] (involving the generation of atomic hydrogen) for the base-catalyzed decomposition of alkyl hydroxymethyl peroxides, but is analogous to the mechanism of decomposition of bis-(hydroxymethyl) peroxide (involving the generation of molecular hydrogen) proposed by Wieland and Wingler.[5] It is postulated that the *n*-butyraldehyde produced is immediately consumed by reaction with more *n*-butyl hydroperoxide according to eq. 10. Thus only a small steady state concentration of either the aldehyde or the intermediate *n*-butyl 1-hydroxybutyl peroxide builds up. Once the initiation period is over the rate-determining step is the decomposition of the intermediate (eq. 11). The aldehyde acts as a catalyst for the decomposition and the summation of eq. 10 and 11 is eq. 1.

The following is a summary of the evidence which supports this postulated sequence for the decomposition of *n*-butyl hydroperoxide to butyric acid and hydrogen: (a) The reaction has an induction period which is eliminated by the addition of aldehydes but not by the addition of ketones.[3] *n*-Butyl hydroperoxide reacts rapidly with aldehydes to give peroxyhemiacetals but not with ketones *vide infra*. (b) The decomposition of *n*-butyl hydroperoxide gives substantially equal amounts of the corresponding butyric acid and hydrogen and only small amounts of butyraldehyde as required by this mechanism. (c) Although this proposed intermediate has not been isolated from the reaction mixture, it has been synthesized and is known to be formed rapidly from *n*-butyraldehyde and *n*-butyl hydroperoxide at room temperature. (d) It has been demonstrated that *n*-butyl 1-hydroxybutyl peroxide decomposes without an induction period at a rate six times that of *n*-butyl hydroperoxide (half-life at 86° of 4 hours as compared to 24 hours). (e) This rate of decomposition is the same within experimental error as that found for the decomposition of *n*-butyl hydroperoxide when *n*-butyraldehyde is added. (f) The decomposition of the intermediate *n*-butyl 1-hydroxybutyl peroxide gives butyric acid, butyraldehyde and hydrogen as qualitatively required by this mechanism. (g) Conducting the decomposition in a fused silica bulb instead of a Pyrex bulb appreciably changed neither the rate of decomposition nor the qualitative and quantitative nature of the products, but conducting the decomposition photochemically at 35° greatly reduced the yield of hydrogen and bu-

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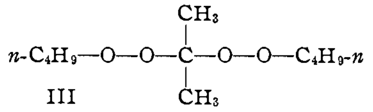
(16) N. A. Milas in Kirk Othmer's "Encyclopedia of Chemical Technology," Vol. 10, Interscience Encyclopedia Inc., New York, N. Y. 1953, p. 63.

(17) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 273 (1946).

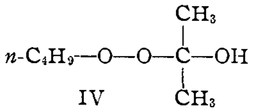
tyric acid indicating that these do not arise from the homolytic cleavage of the O–O bond. The evidence implicating *n*-butyl 1-hydroxybutyl peroxide as the intermediate in the uncatalyzed thermal decomposition of liquid *n*-butyl hydroperoxide to give butyric acid and hydrogen is substantial.

The next problem to be considered is the precise mechanism whereby the *n*-butyl 1-hydroxybutyl peroxide undergoes decomposition, *i.e.*, the mechanism for the reaction represented by eq. 11. In order to investigate the effect of the structure of the 1-hydroxyalkyl group on the decomposition of peroxides of this type, *n*-butyl hydroxymethyl and *n*-butyl 1-hydroxyethyl peroxides were prepared (eq. 10, R = –H and –CH_3). *n*-Butyl hydroperoxide did not react with acetone on simple mixing, but in the presence of a trace of mineral acid the peroxyketal III was formed instead of the peroxyhemiketal IV. This is analogous to the results reported for the reaction of *t*-butyl hydroperoxide with aldehydes and ketones[14,18] and it was therefore not possible for us to include an example of type IV in our study.



$$n\text{-}C_4H_9\text{—O—O—}\overset{CH_3}{\underset{CH_3}{C}}\text{—O—O—}C_4H_9\text{-}n$$

III



$$n\text{-}C_4H_9\text{—O—O—}\overset{CH_3}{\underset{CH_3}{C}}\text{—OH}$$

IV

The products from the decomposition of *n*-butyl hydroxymethyl peroxide are reported in Table I. The rate of its decomposition was approximately four times that for *n*-butyl 1-hydroxybutyl peroxide and the yield of hydrogen was 77% as compared to 52–54%. An equal molar ratio of butyraldehyde, formic acid and hydrogen is predicted according to equation 11; that found was 34:41:77. This discrepancy can be rationalized to a considerable extent by assuming subsequent reactions which reduce the yields of butyraldehyde and formic acid.[19] Approximately 15% of the liquid was not identified and this may help account for some of the discrepancy. The low yield of *n*-butyraldehyde can also be explained by the formation of any higher molecular weight material such as a polymer or an acetal which would not be detected by the gas partition chromatography method of analysis.

n-Butyl 1-hydroxyethyl peroxide decomposed to give the products reported in Table I. However, the ratio of butyraldehyde, acetic acid and hydrogen was 13:19:42. Again this can be reconciled with the theory by assuming loss of butyraldehyde and acetic acid in subsequent reactions. The formation of butyl butyrate and butyric acid is of special interest. These are products characteristic of the decomposition of butyl hydroperoxide and *n*-butyl 1-hydroxybutyl peroxide. It has been shown that reaction 10 is an equilibrium[18] and this suggests that some of the *n*-butyl hydroperoxide resulting from the reversal of this reaction combines with *n*-butyraldehyde to give the intermediate *n*-butyl 1-hydroxybutyl peroxide which then undergoes decomposition according to eq. 11.

In the presence of toluenesulfonic acid, *n*-butyl 1-hydroxybutyl peroxide decomposes but gives only one-fifth as much hydrogen as in the absence of acid indicating that the hydrogen-forming reaction is not acid-catalyzed. *n*-Butyl 1-hydroxyethyl and 1-hydroxybutyl peroxides decomposed rapidly in the presence of base, but in contrast to *n*-butyl hydroxymethyl peroxide[8,18] no appreciable amount of gas was evolved. It therefore appears that the structural requirement for the hydrogen-forming, *base-catalyzed*, decomposition is a hydroxymethyl peroxy group, –$OOCH_2OH$.

The fact that *n*-butyl deuteroperoxide gives no HD or D_2 on decomposition,[3] and that there is no HD or D_2 formed[10b] when the Blank–Finkenbeiner reaction is conducted in D_2O, is added evidence that only the hydrogens attached to the peroxidic carbon atoms are involved in the hydrogen evolution process.

Rieche[8] and Wieland and Wingler[5] used the decolorization of methylene blue solutions as a diagnostic test for atomic hydrogen. Qualitative observations on the relative rates of decolorizing the same methylene blue solution are recorded in Table II.

TABLE II

RATES OF DECOLORIZATION OF METHYLENE BLUE SOLUTION

Reagent	Micro-moles	Time for decolorization At 25°[a]	At 86°[a]	At 86°[b]
n-BuOOH	890	(–)[c]	4–5 hr.	3–5 hr.
t-BuOOH	890	(–)[c]	(–)[c]	8–15 hr.
n-BuOOCHOH-*n*-Pr	500	(–)[c]	(–)[c]	1 hr.
CH_2O, H_2O_2, NaOH[d]		(–)[c]	(–)[c]	2 hr.[d]
$CoCl_2$, KCN[e]	192	10 sec.[f]	3 sec.[f]	...
Zinc, HCl[g]	770	25 sec.[f]	10 sec.[f]	...

[a] Methylene blue concentration, 20 mg./l.; 2 ml., 0.10 micromole, was used. [b] Methylene blue concentration, 10 mg./l.; 2 ml., 0.05 micromole, was used. [c] A negative reaction indicates no decolorization after 36 hours. [d] This is the Blank–Finkenbeiner reaction.[4] Wieland and Wingler[5] reported that this did not decolorize methylene blue solution. A mixture of 0.1 ml. of 30% hydrogen peroxide, 0.2 ml. of 37% formaldehyde solution and 2 ml. of methylene blue solution was prepared and the sodium hydroxide was added. The decolorization which did occur at 86° with the more dilute solution was long after the hydrogen evolution had ceased. [e] This solution of potassium cobaltocyanide was made by mixing 0.1 ml. each of a solution of 2.5 g. of cobaltous chloride in 10 ml. of water and 2.5 g. of potassium cyanide in 5 ml. of water. [f] The decolorization was so rapid that the rate of mixing was probably the determining factor. [g] This was 50 mg. of zinc dust and 0.2 ml. of 6 *N* hydrochloric acid.

Two of the hydrogen evolution reactions reported in Table II decolorized the methylene blue solutions in a matter of *seconds*, namely, the reaction of potassium cobaltocyanide with water and the reaction of zinc dust with hydrochloric acid. All of the peroxide decompositions, including a control using *t*-butyl hydroperoxide which evolves oxygen instead of hydrogen,[20] decolorized the methylene blue solution only after a period of *hours* at 86° when very dilute methylene blue solution was

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[18] T. H. Dickey, J. H. Raley, F. F. Rust, R. S. Tresede and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949); F. H. Dickey, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **71**, 1432 (1949).

[19] See note 15 concerning a further statement about the similar discrepancy in the butyl 1-hydroxybutyl peroxide.

[20] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946).

used. In these experiments the peroxides were in excess of the methylene blue by a factor 10^3 to 10^4 molar. It seems logical to assume on this basis that the peroxide decompositions in experiments 1, 3 and 4 (Table II) do not generate atomic but molecular hydrogen.

An additional and perhaps more specific test for atomic hydrogen is the hydrogen–deuterium exchange reaction.[21] The reaction of hydrogen atoms with deuterium gas $H\cdot + D_2 \rightarrow HD + D\cdot$ has a rather low energy of activation, about 7 kcal./mole,[22] yet molecular hydrogen and deuterium do not exchange appreciably under ordinary circumstances. Accordingly, the decompositions of *n*-butyl hydroperoxide and *n*-butyl 1-hydroxybutyl peroxide were conducted under standardized conditions in a deuterium atmosphere. These results were compared to a blank of hydrogen, deuterium and *t*-butyl hydroperoxide, which is known to evolve no hydrogen on decomposition,[20] and a control containing cobaltocyanide ion which almost certainly reacts with water to evolve hydrogen in atomic form.[23]

During the reaction of potassium cobaltocyanide with water there was in the order of fifty times more exchange between the hydrogen evolved and the deuterium added than during the decomposition of the peroxides reported in experiments 1, 2, 3 and 4 (Table III). Furthermore there was approximately the same amount of exchange in the blank containing *t*-butyl hydroperoxide. One can logically conclude on the basis of this evidence that the peroxide decompositions do not generate atomic hydrogen.[24]

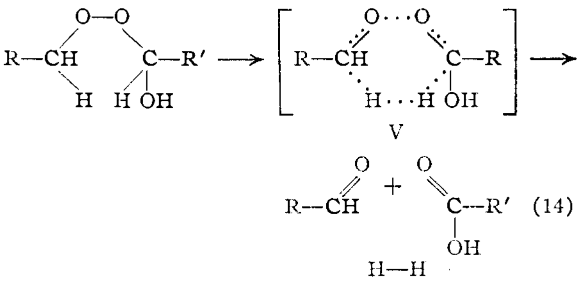
TABLE III

DEUTERIUM EXCHANGE EXPERIMENTS

Reagents	Isotope ratio H_2, %	D_2, %	HD, %	% HD produced[a]	HD/D_2 ratio[b]
n-$C_4H_9OOH + D_2$	40.7	58.0	1.25	0.05	0.001
Blank	0.07	97.9	2.0		
i-$C_4H_9OOH + D_2$	79.2	19.7	1.05	.08	.004
Blank	0.25	95.0	4.7		
t-$C_4H_9OOH + H_2 + D_2$	71.0	27.7	1.27	.10	.004
Blank	72.6	26.2	1.17		
n-$C_4H_9OOCHOHC_3H_7$-*n* + D_2[c]	37.7	61.5	0.80	.25	.004
n-$C_4H_9OOCHOHC_3H_7$-*n* + D_2[d]	83.4	16.4	0.26	.11	.007
Blank	0.00	99.1	0.89		
$K_4Co(CN)_6 + H_2O + D_2$	58.8	33.8	7.41	6.71	.20
$K_4Co(CN)_6 + H_2O + D_2$	80.0	16.3	3.74	3.41	.21
Blank	0.07	97.9	2.03		

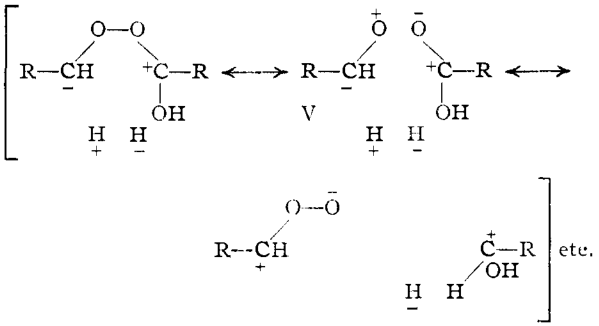
[a] This is a corrected value for the % HD present at the end of the experiment in excess of the % HD which would be present from that in the deuterium added as measured in the blank. These corrected HD values are subject to an analytical error of about ±0.04%. [b] These ratios have an inherent error of about 0.002%. [c] This experiment was on the neat liquid. [d] This experiment was conducted in aqueous solution to simulate the conditions of the cobaltocyanide experiment more closely.

Based on the above evidence we wish to propose mechanism (14) for the thermal decomposition of *n*-butyl 1-hydroxybutyl peroxide and related compounds into hydrogen, a carboxylic acid and aldehyde.



(14)

The transition state V represented in brackets affords a lower energy of activation than the homolytic cleavage of the peroxide bond. This results from the concerted nature of the reaction and the fact that this transition state is stabilized by various hyperconjugated forms.



This proposed mechanism requires that the reaction follow first-order kinetics. A detailed study of the kinetics of this reaction and of deuterium isotope effects on suitably deuterated derivatives is currently under investigation.

The reaction leading to the esters in these decompositions (eq. 12) accounted for 20–25% of the starting alkyl 1-hydroxyalkyl peroxide. Thus *n*-butyl 1-hydroxybutyl peroxide gave *n*-butyl butyrate (24%), *n*-butyl 1-hydroxyethyl peroxide gave *n*-butyl acetate (22%), and *n*-butyl hydroxymethyl peroxide gave *n*-butyl formate (22%). Very little is known concerning the mechanism of this reaction other than it appears to be acid-catalyzed as evidenced by the observation that in the presence

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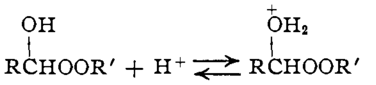
[21] We are indebted to Dr. Richard A. Ogg for suggesting this test and for valuable discussions concerning these experiments. See M.S. thesis of Donald P. Hollis, Stanford University, May, 1956.

[22] R. C. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., second edition, Vol. II, New York, N. Y., 1954.

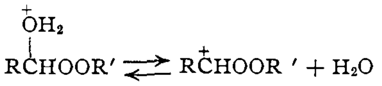
[23] Private communication, R. A. Ogg. The hexacyanocobaltate-(II) ion has a total of 37 electrons; the stable electronic arrangement is 36. Thus there is a strong tendency to lose one electron in a reaction with water or better with a proton to give a hydrogen atom and the stable hexacyanocobaltate(III) ion, $Co(CN)_6^{-4} + H^+ \rightarrow Co(CN)_6^{-3} + H$.

[24] These experiments are admittedly complicated by the fact that the deuterium is primarily in the gas phase and the hydrogen is generated in the liquid phase. Therefore the actual exchange may be controlled by the rate of diffusion of deuterium in solution. It is felt that the evidence from the controls is sufficient to rule out complications in this respect. It is possible that atomic hydrogen is generated, but instead of exchanging with deuterium, which may be present in low concentration in the liquid, reacts with some liquid component. The reaction of aldehydes with hydrogen atoms $RCHO + H\cdot \rightarrow RC{=}O + H_2$ is known to have a low energy of activation[22] and would thus be competitive with the deuterium exchange reaction. Acyl radicals give carbon monoxide and alkyl radicals; products to be expected from such a course of decomposition are not found in significant amounts.

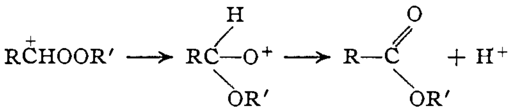
of toluenesulfonic acid both *n*-butyl hydroperoxide and *n*-butyl 1-hydroxybutyl peroxide gave a higher yield of butyl butyrate. It seems unlikely that this is a simple acid-catalyzed esterification since the yield of hydrogen is at the same time greatly reduced. It may be a rearrangement initiated by oxonium ion formation somewhat similar to the Baeyer–Villiger peroxidic oxidation of ketones[25] or the Criegee rearrangement of peroxy esters[26] as indicated by the equations



$$\overset{\displaystyle OH}{R\underset{|}{C}HOOR'} + H^+ \rightleftarrows \overset{\displaystyle \overset{+}{O}H_2}{R\underset{|}{C}HOOR'} \qquad (15)$$



$$\overset{\displaystyle \overset{+}{O}H_2}{R\underset{|}{C}HOOR'} \rightleftarrows R\overset{+}{C}HOOR' + H_2O \qquad (16)$$



(17)

Acknowledgment.—We wish to thank the California Research Corporation for generous support which made these investigations possible.

Experimental[27]

***n*-Butyl 1-Hydroxybutyl Peroxide.**—*n*-Butyl hydroperoxide (3.9 g., 0.054 mole, $n^{25}D$ 1.4051) and freshly distilled butyraldehyde (4.8 g., 0.054 mole), were mixed with cooling in a small distilling flask. After 0.5 hour the mixture was distilled; b.p. 34–37° (1 mm.), $n^{20}D$ 1.4197, 6.3 g. (72%).

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.23; H, 11.18. Found: C, 58.57; H, 11.24.

***n*-Butyl 1-Hydroxyethyl Peroxide.**—*n*-Butyl hydroperoxide and acetaldehyde were allowed to react in the same manner and the product distilled; b.p. 30–31.5° (1 mm.), 75% yield, $n^{20}D$ 1.4104.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.32; H, 10.37.

***n*-Butyl hydroxymethyl peroxide** was made by the method reported for the *t*-butyl isomer.[18] *n*-Butyl hydroperoxide (2.37 g., 0.026 mole) was cooled to 5° and formaldehyde (2.24 g., 36–38% solution, 0.27 mole) was added. After 0.5 hour the solution was warmed to 35°, a few grams of anhydrous sodium sulfate and a few milliliters of benzene were added and the benzene layer was separated, dried over sodium sulfate and distilled; b.p. 55–56.5° (8 mm.), 2.32 g. (72%) $n^{20}D$ 1.4172.

Anal. Calcd. for $C_5H_{12}O_3$: C, 49.98; H, 10.07. Found: C, 49.98; H, 10.11.

Decompositions: Apparatus, Procedure, Analyses.—The apparatus and procedure employed for the peroxide decompositions and analyses of both gas and liquid portions were identical with those described in the preceding paper.[3] The details for the decompositions are given in Tables I and IV.

Methylene Blue Experiments.—To each of six test-tubes in a heated oil-bath at 86° containing 2 ml. of a 0.0002% solution of methylene blue was added 0.1 ml. of the reagent being studied. The times for decolorization of the solution are given in Table II.

Deuterium–Hydrogen Exchange Experiments.—In these experiments a liquid-phase hydrogen-forming reaction was conducted in an atmosphere of deuterium and the resultant gas mixture analyzed for the percentage of H_2, HD and D_2. The decompositions were conducted in a closed system composed of a pressure stopcock with one arm sealed off giving a bulb of approximately 4-ml. capacity. The sample to be decomposed was introduced with a capillary pipet; the tube was evacuated at a vacuum line while the sample was cooled to −75°. It was then filled with deuterium gas (or a mixture of hydrogen and deuterium in the case of the *t*-butyl hydroperoxide decomposition) to the desired pressure. The tube was removed from the vacuum line, attached to a constant speed motor and immersed in a bath at 86° for approximately 60 hours. The gas was then transferred to a sampling bulb for mass spectrographic analyses.[27] In the case of the potassium cobaltocyanide experiments the tube was modified to permit loading the cobaltous chloride solution (0.1 ml. containing 0.05 g. of cobaltous chloride) to a very small side arm and the potassium cyanide solution (0.2 ml. containing 0.10 g. of potassium cyanide) to the bottom of the tube. The tube was evacuated, filled with deuterium to one atmosphere pressure, sealed and the reagents mixed at the time the tube was immersed into the constant temperature bath. The deuterium used in these experiments was generated from 99.5% D_2O by reaction with sodium. It always contained a small amount of HD and a correction was made for the amount of HD in the final gas sample which was due to the HD in the original gas mixture. The results of the analyses are listed in Table III; column 5 gives the ratio of the corrected HD value after the reaction to the total amount of D_2 at the end of the experiment. These values were undoubtedly dependent upon the specific experimental conditions, but every effort was made to keep the conditions strictly comparable.

TABLE IV

n-BUTYL 1-HYDROXYALKYL PEROXIDE DECOMPOSITIONS

Compound decomposed and conditions C_4H_9–OO–CHOHR, R =	Temp., °C.	Sample Weight, g.	Sample Mole	Total gas vol., ml./S.T.P.	Liquid residue weight, g.	Half-life,[g] $T_{1/2}$, hours
n-C_3H_7[a]	86	1.105	0.0068	119.2	1.00	4.1
n-C_3H_7[a] (quartz)[b]	86	0.826	.0051	91.5	0.75	4.6
n-C_3H_7[a] (u.v. light)[c]	35	.863	.0053	54.0	.76	
n-C_3H_7 (0.05 g. TSA)[d]	86	.500	.003	18.7	.45	6.1
H[e]	86	.682	.0057	108.8	.62	0.9
CH_3[f]	86	1.143	.0085	121.5	.98	9.5

[a] *n*-Butyl 1-hydroxybutyl peroxide. All decompositions were conducted on the neat liquid. Unless stated otherwise all decompositions were conducted in a Pyrex bulb. [b] This decomposition was conducted in a fused silica bulb. [c] This decomposition was conducted in a fused silica bulb and was irradiated by the ultraviolet light from a Mineralight Lamp, model V43, 2536 Å., manufactured by Ultraviolet Products Inc., Los Angeles, Calif. [d] This decomposition was catalyzed by 10% of toluenesulfonic acid. The apparatus was so arranged that the toluenesulfonic acid did not come into contact with the liquid until the system had been closed and brought to temperature. [e] *n*-Butyl hydroxymethyl peroxide. [f] *n*-Butyl 1-hydroxyethyl peroxide. [g] The half-life was the time elapsed for one-half of the total volume of gas to be evolved. In no case was there observed an induction period in these decompositions.

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[25] W. E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953).

[26] R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948); see also P. D. Bartlett and J. L. Kice, THIS JOURNAL, **75**, 5591 (1953).

[27] Carbon–hydrogen analyses were by Microchemical Specialties Co., Berkeley, California; mass spectrographic analyses by Stanford Research Institute. All decompositions and distillations of peroxidic materials were conducted behind safety shields constructed of two sheets of safety glass separated by a one-inch air space.